5

Re-distribution of diblock copolymer chains in a mixed micellar solution

Summary

In the previous two chapters the behavior of a single diblock copolymer in solution was discussed, both theoretically and experimentally. The formation of polymolecular micelles was seen to be determined by a balance between enthalpic and entropic factors. In this chapter a micellar mixture of two different diblock copolymers in the presence of a selective solvent is investigated. Each diblock copolymer consists of a polystyrene (PS) block, which has the same molecular weight for both diblock copolymers, and a poly(2-vinylpyridine) (PVP) block of which the molecular weight is different. In this way, the possibility of the formation of mixed micelles is created, where both types of chains form one polymolecular micelle. Indeed, it is seen that upon dissolution there is a rapid formation of polymolecular micelles. The micelles formed have rather variable sizes at this initial stage. However, after a considerable aging time the block copolymers seem to have re-equilibrated in solution towards their most favorable micellar state and an almost perfect bi-modal size distribution is obtained. A theoretical explanation for the formation of this almost bi-modal distribution is given on the basis of free energy calculations for 'pure' and mixed polymolecular micelles.

The work described in this chapter is submitted to *Macromolecules*

5.1 Introduction

In the previous chapters, the behavior of diblock copolymer in a selective solvent was investigated. It was shown that (polymolecular) micelles were formed instantaneously, but that the true equilibrium state was reached only after re-equilibration of the system. The solutions all consisted of one type of diblock copolymer as in many previous experimental and modeling studies of block copolymers systems in dissolved or solid state.[1-13]

However, there is only a small number of studies dealing with mixtures of diblock copolymers in solution.[14-19,8] In this chapter, the study of diblock copolymer mixtures in selective solvent will be presented. It will be shown that time is again an important variable, considering the slow dynamics of the system. The equilibrium structure and sizes of the block copolymer micelles are reached only slowly.

5.2 Diblock copolymer mixture

Two different diblock copolymers, PS-PVP 75-18 and PS-PVP 75-102, of which the characteristics are presented in table1-1, were used. Both block copolymers were dissolved simultaneously in toluene. The concentration of the solution obtained was 1 wt%, while the weight ratio between both diblock copolymers was 1:1.

The structures formed by the diblock copolymer mixture were studied by means of transmission electron microscopy. To obtain a suitable specimen, a small droplet of the solution was placed on a carbon-coated copper microscopy grid. Most of the solution was then removed by blotting with filter paper. In this way it is possible to obtain a micellar layer which is thin enough to be studied in the electron microscope. A small amount of iodine was added to the solution just before it was placed on the grid for staining purposes.

Ideally, the specimen to be investigated would consist of a monomicellar layer. This result, however, can only be obtained occasionally. Due to the blotting technique used for the preparation of a sufficiently thin specimen it was not possible to obtain the same thickness for each specimen. In spite of this experimental limitation it is possible to compare the formation and behavior of the block copolymer micelles in solution as a function of time.

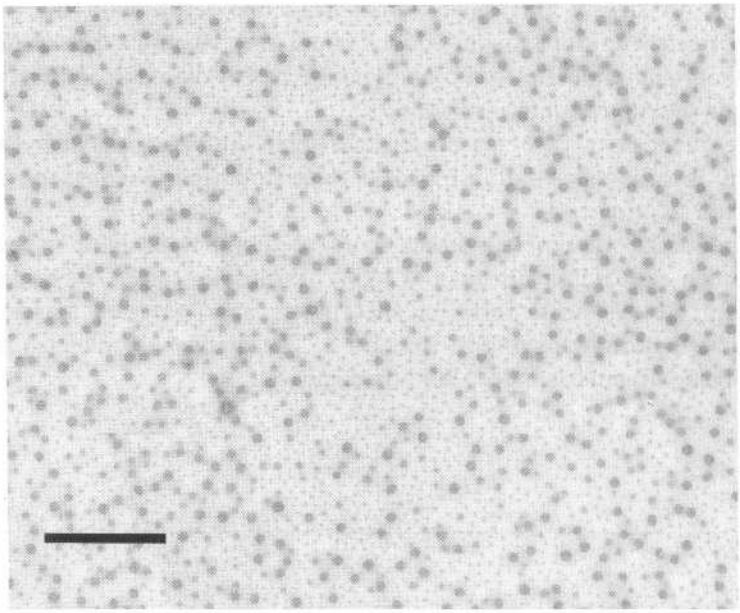

Figure 5-1. *Electron micrograph of a mixture of PS-PVP 75-18 and PS-PVP 75-102 diblock copolymers after 1 hour of aging. The scale bar indicates 500 nm.*

5.3 Evolution of mixed micelles towards a bi-modal distribution

Figure 5-1 shows an electron micrograph of a mixture of the two types of PS-PVP block copolymers used. The polymolecular micelles are clearly visible as spheres. From this figure it is obvious that the micelles formed cover a broad range of sizes. There are small micelles having a diameter of about 15 nm, but much larger micelles having a diameter of about 45 nm are also visible. This latter size is also found in previous experiments where the behavior of the PS-PVP 75-102 diblock copolymer was investigated (see chapter 2).[9,20] However, it is true that the sizes found here cannot be compared quantitatively with those found in the previous chapters, since in the experiments described here, the micelles are not in their native (dissolved) state anymore.[(1)]

Figure 5-2 shows a frequency histogram of the diameters of the micelles visible in figure 5-1. From this representation it is clear that the micelles formed differ

[(1)] Still, the values of the sizes are almost equal. This is probably due to two opposing effects: (1) Because of the fact that all toluene has been removed, the micelles will probably flatten somewhat on the carbon support film. (2) Upon removal of the toluene, there may be some deswelling of the cores.

considerably in size at this stage. Comparing this result with the polymolecular micelles formed within the single diblock copolymer solutions (see chapter 2 and 3), suggests that mixed micelles comprising both types of diblock copolymers must have been formed yielding an intermediate size.

However, as was the case with the single diblock copolymer solutions, true equilibrium is only reached after a considerable time. This becomes clear after aging of this mixed solution.

The mixed solution was stored in a sealed bottle at room temperature. Figure 5-3 shows the result after 38 days of aging. From this figure, there seems to be a tendency for the system to form micelles having less variation in size. Figure 5-4 shows the histogram belonging to figure 5-3. The number of micelles having a size between 30 and 40 nm has indeed slightly decreased.

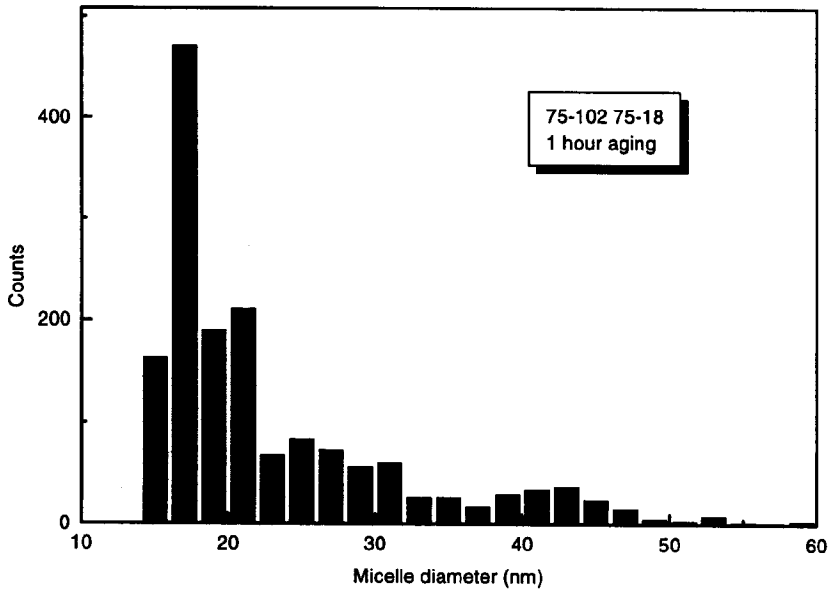

Figure 5-2. *Histogram showing the size distribution corresponding to figure 5-1.*

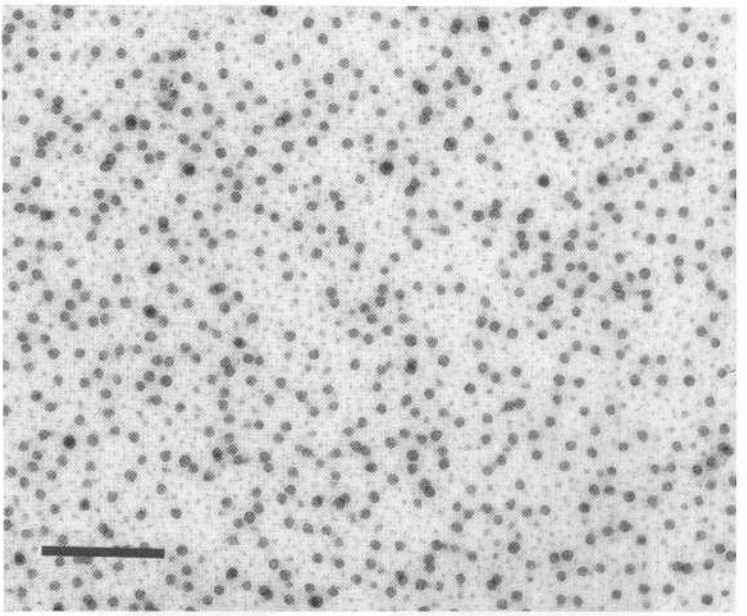

Figure 5-3. *Electron micrograph of a mixture of PS-PVP 75-18 and PS-PVP 75-102 diblock copolymers after 38 days of aging. The scale bar represents 500 nm.*

This evolution towards a smaller variation in size is even more clearly demonstrated by figures 5-5 and 5-6. Here, an electron micrograph and corresponding size distribution histogram of the same starting solution after aging for 4 months are shown. Comparing figure 5-5 with figures 5-1 and 5-3 shows that the block copolymer mixture in solution forms two micellar populations, which differ in size. The process leading to a bi-modal distribution has continued and as a result two sizes of micelles are detected. This, again, is clearly visible in figure 5-6 where the size distribution histogram after 4 months of aging is shown.

These results show that the micelles that are formed initially (figure 5-1), obviously do not represent the most favorable form, i.e. the equilibrium state. As has been discussed in chapters 2 and 3[9,20] the formation of micelles by block copolymers upon dissolution in a selective solvent is a very rapid process. These initial micelles (which are in a sort of quasi-equilibrium state) are formed by an enthalpy-driven process because of the very unfavorable interactions between toluene and PVP units and between PS and PVP blocks. The real equilibrium structures, however, which can

be considerably larger, are formed much slower. Only after a considerable time, diblock copolymer micelles reach their most favorable state.

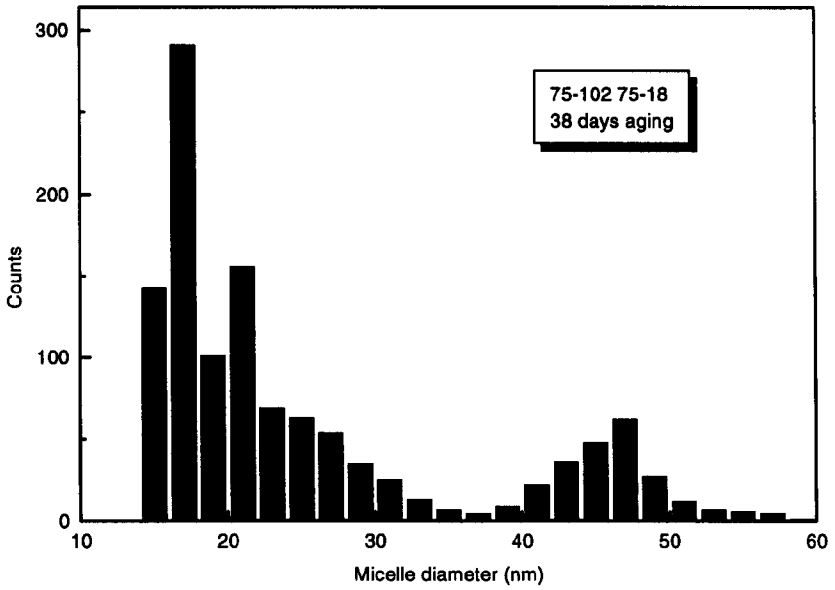

Figure 5-4. *Histogram showing the size distribution corresponding to figure 5-3.*

The experiments described here support the idea of the very fast formation of quasi-equilibrium micelles in the initial stage. Both diblock copolymers participate in the rapid formation of polymolecular micelles upon dissolution in toluene, because of the unfavorable interactions between the PVP blocks and toluene. This results in micelles built up from two diblock copolymers differing in length, and hence a broad size distribution for the polymolecular micelles is formed.

In solutions of block copolymers there is a continuous exchange of chains between polymolecular micelles. This exchange will finally lead to the formation of the most stable state. The formation of such a stable state obviously also takes place in the mixture of diblock copolymers in solution, as figures 5-3 and 5-5 show.

From figure 5-5 the appearance of larger micelles is clearly visible. This process of growth of polymolecular micelles was discussed in chapter 4 and confirms the idea that the micelles formed directly upon dissolution are not in their most favorable state. Although here a mixture of block copolymers is studied, the two sizes of polymolecular micelles visible in figure 5-5 compare very well with previous

values found for the respective diblock copolymers studied separately in dissolved state (see chapters 2 and 4).[20,21] There, an average size for the PS-PVP 75-102 and PS-PVP 75-18 cores of about 50 and 15 nm, respectively, was found. The reason why the values of the total micellar diameter found here and the values of the micellar core diameter found in chapters 2 and 4 are almost equal has been explained above. It is worth noting that the average size of micelles formed by PS-PVP 75-18 (≈15 nm) is somewhat less than the average size found here for the 'small' micelles (≈23 nm).

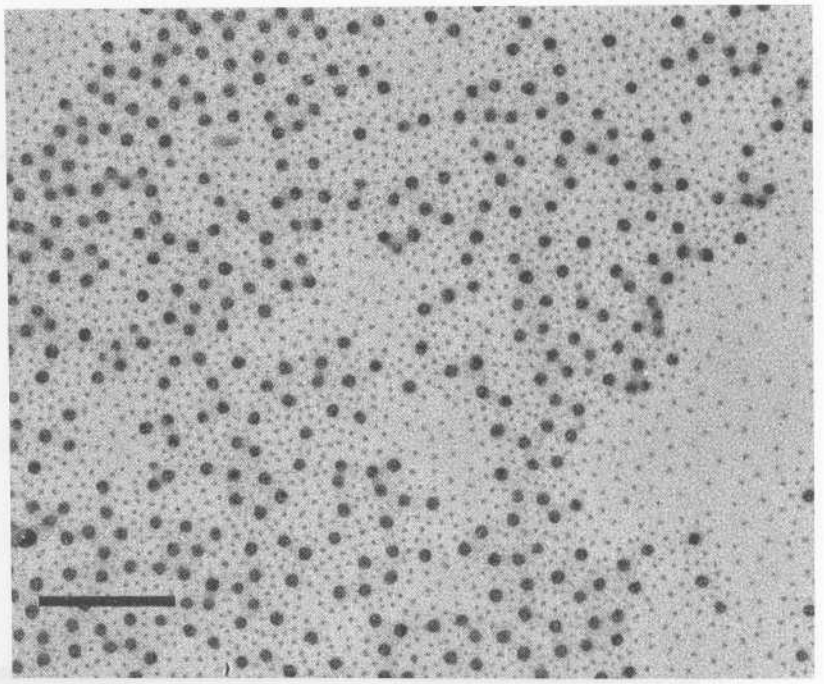

Figure 5-5. *Electron micrograph of a mixture of PS-PVP 75-18 and PS-PVP 75-102 diblock copolymers after 4 months of aging. Scale bar represents 500 nm.*

The size distribution plots given in figures 5-2 and 5-4 should represent a rather unfavorable situation indeed. A large number of copolymer chains is consumed during the formation of micelles having a size that does not compare with one of the final sizes. For the formation of the final structures, there will be two processes involved which will cooperate with each other. First, there is the continuous exchange of copolymer chains. This means that, a 'short' (PS-PVP 75-18) or 'long' (PS-PVP 75-102) copolymer chain might occasionally be expelled from a mixed polymolecular micelle. The probability for one type of the chains to be expelled, will depend on the

size of such a polymolecular micelle at that very moment. Secondly, there is also a growth mechanism involved in the evolution towards equilibrium. This means that a polymolecular micelle built from, for example, PS-PVP 75-102 copolymer chains will contain more chains in the final polymolecular micelle than in the initially formed polymolecular micelle. These two processes will cooperate. When a 'short' (PS-PVP 75-18) copolymer chain is expelled from a rather large polymolecular micelle, it will eventually be replaced by a 'long' (PS-PVP 75-102) copolymer chain forming a micelle closer to the equilibrium structure.

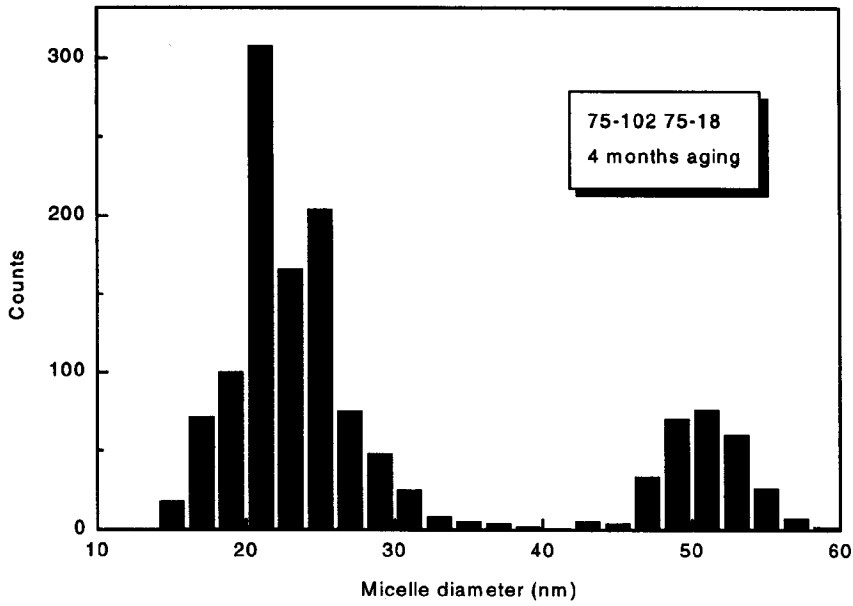

Figure 5-6. *Histogram showing the size distribution corresponding to figure 5-5.*

The process of micellar growth as discussed above, finally results in an equilibrium distribution of micellar sizes. The equilibrium properties of polymer micelles that are formed in the diblock copolymer mixture are analyzed theoretically in the next paragraph by considering the free energy of micelles in solution taking into account the possibility of the formation of mixed micelles.

5.4 Free energy of micelles formed from a diblock copolymer mixture in solution

To calculate the free energy of the mixture it is assumed that three types of micelles can be formed: 'pure' PS-PVP 75-18 (denoted *A*-micelles), 'pure' PS-PVP 75-102 (denoted *C*-micelles) and mixed *A/C* micelles. The blocks *A* and *C* represent the PVP blocks of the block copolymers described in this chapter, $N_A \leq N_C$. The PS-block in both copolymers is identical and is denoted as the *B*-block. The polymerization index of the *B*-block is given by N_B. For the sake of simplicity, only identical mixed micelles are considered. The derivations are given for any mixture of two types of diblock copolymers, but will be applied more explicitly to the system described above.

Assuming the number of free chains of both block copolymers constant, the equilibrium properties of the polymolecular micelles in solution can be defined by analyzing the free energy (in units of kT):

$$F = \Pi_A^{mic}(F_A + \ln \phi_a^{mic}) + \Pi_C^{mic}(F_C + \ln \phi_c^{mic}) + \Pi_{mix}^{mic}(F_{mix} + \ln \phi_{mix}^{mic}) \quad (5\text{-}1)$$

where Π_i^{mic} and ϕ_i^{mic} are the number and volume fractions of micelles of type i ($i = A$, C, *mix*) respectively and F_i is the corresponding free energy of the micelles. The logarithmic terms in equation 5-1 represent the translational entropy of the micelles. The contribution of these terms is smaller than that of the other terms, but it can be important to take them into account for the determination of the fraction of mixed micelles in solution

The number of micelles in the solution is connected with the number of chains and the aggregation numbers of the micelles n_i:

$$\Pi_A^{mic} \equiv \frac{\Pi_{AB}^0 - \Pi_{AB}}{n_A} \qquad \Pi_C^{mic} \equiv \frac{\Pi_{CB}^0 - \Pi_{CB}}{n_C} \qquad \Pi_{mix}^{mic} \equiv \frac{\Pi_{AB} + \Pi_{CB}}{n_{mix}} \quad (5\text{-}2)$$

where $\Pi_{iB}{}^0$ is the total number of chains of type i ($i = A,C$) ($\Pi_{iB}{}^0 \equiv \phi_{iB} V / (N_i + N_B)$, where ϕ_{iB} is the volume fraction of polymer of type i), Π_{iB} is the number of corresponding chains forming mixed micelles and V is the volume of the system.

The free energy (in units of kT) of a "pure" micelle of type i ($i = A,C$) can be written in a standard way:[22,23]

$$F_i = F_{surf} + F_{ext} = c_1 n_i^{2/3} (N_i \upsilon)^{2/3} \frac{\gamma}{kT} + c_2 n_i^{3/2} + c_3 n_i^{5/3} (N_i \upsilon)^{-1/3} \qquad (5\text{-}3)$$

where γ is the interfacial tension of micelles, describing the incompatibility of the PVP blocks with the solvent and PS blocks, c_j are numerical coefficients and υ is the volume of a monomer.

The first term in equation 5-3 represents the surface free energy, while the last two terms are connected with the free energy of extension of the PS or PVP blocks in the corona and core region respectively. The extension of the PS blocks in the corona influences the properties of the micelles more than the extension of the PVP blocks in the core region.[22] This means that the equilibrium size of a micelle is determined mainly by the balance between surface free energy and the free energy of the PS block extension in the corona region.

The free energy of a mixed micelle can be calculated in a similar way as for the 'pure' micelles, taking into account the relation between the radius of the micelle and the aggregation number, which is given by:

$$\frac{4\pi}{3} R_{mix}^3 = (n_{AB}^{mix} N_A + n_{CB}^{mix} N_C)\upsilon = n_{mix} N_A \upsilon (1 + \frac{n_{CB}^{mix}}{n_{mix}} (\frac{N_C}{N_A} - 1)) \qquad (5\text{-}4)$$

$$n_{mix} = n_{AB}^{mix} + n_{CB}^{mix} \qquad (5\text{-}5)$$

where $n_{AB}{}^{mix}$ and $n_{CB}{}^{mix}$ are the aggregation numbers of *A-B* (PS-PVP 75-18) and *C-B* (PS-PVP 75-102) copolymers in a mixed micelle.

Since it is supposed that all mixed micelles are identical, the fraction of *C-B* copolymer chains in a mixed micelle is connected with the total fraction of chains forming mixed micelles:

$$\frac{n_{CB}^{mix}}{n_{mix}} = \frac{\Pi_{CB}}{\Pi_{AB} + \Pi_{CB}} \qquad (5\text{-}6)$$

When there are no 'pure' micelles in solution, the fraction of *C-B* chains in a mixed micelle is determined by the total fraction of *C-B* chains in the system:

$$\frac{n_{CB}^{mix}}{n_{mix}} = \frac{\Pi_{CB}^{0}}{\Pi_{AB}^{0} + \Pi_{CB}^{0}} \tag{5-7}$$

The free energy of a mixed micelle can then be written (in units of kT) as:

$$F_{mix} = F_{surf} + F_{ext} = c_1 n_m^{2/3} \upsilon^{2/3} N_{eff}^{2/3} \frac{\gamma}{kT} + c_2 n_{mix}^{3/2} + c_3 n_{mix}^{5/3} \upsilon^{-1/3} N_{eff}^{-1/3} \tag{5-8}$$

where

$$N_{eff} = N_A \left[1 + \frac{\Pi_{CB}}{\Pi_{AB} + \Pi_{CB}} \left(\frac{N_C}{N_A} - 1 \right) \right] \tag{5-9}$$

and can be considered as an 'effective' length (number of monomer units) of an 'averaged' block taking part in forming a mixed micelle.

From equation 5-1 the free energy of the polymer system is seen to be a function of five variables, the aggregation numbers of micelles n_A, n_B and n_{mix} and the fraction of *A-B* and *C-B* chains forming the mixed micelles. Minimization of the free energy leads to the equilibrium values of these variables. According to these calculations, the size of a 'pure' micelle is the same as in a solution of only *A-B* or *C-B* block copolymer chains:

$$R_{AB} \sim (N_A \upsilon)^{3/5} \left(\frac{\gamma}{kT} \right)^{2/5}$$

$$R_{CB} \sim (N_C \upsilon)^{3/5} \left(\frac{\gamma}{kT} \right)^{2/5} \tag{5-10}$$

The size and aggregation number of a mixed micelle are given by:

$$R_{mix} \sim (N_{eff} \upsilon)^{3/5} \left(\frac{\gamma}{kT} \right)^{2/5}$$

$$n_{mix} \sim (N_{eff} \upsilon)^{4/5} \left(\frac{\gamma}{kT} \right)^{6/5} \tag{5-11}$$

The difference between mixed and 'pure' micelles is only the length, N_{eff}, of an 'averaged' chain forming a mixed micelle:

$$\frac{N_{eff}}{N_A} = \frac{N_C}{N_A}\left[\frac{2}{5}\frac{1-\frac{N_A}{N_C}}{1-(\frac{N_A}{N_C})^{2/5}}\right]^{5/3} \tag{5-12}$$

In the limit where the long chain (*C-B*) has almost the same length as the short chain (*A-B*) ($N_C \rightarrow N_A$), the effective length N_{eff} approaches N_A. If the difference in chain length between the *A* and *C* block is large, the fraction of *C-B* copolymer in a mixed micelle;

$$\frac{n_{CB}^{mix}}{n_{mix}} = \frac{\Pi_{CB}}{\Pi_{AB}+\Pi_{CB}} = \frac{N_{eff}-N_A}{N_C-N_A} \tag{5-13}$$

tends to $(2/5)^{5/3}$. This means that only a few *C-B* blocks form a mixed micelle. Furthermore, the 'effective' length is somewhat larger than N_A. This is also true for the intermediate range of block lengths. Consequently, the size of a mixed micelle is somewhat larger than that of a 'pure' *A-B* micelle:

$$\frac{R_{mix}}{R_{AB}} \sim (\frac{N_{eff}}{N_A})^{3/5} \sim (\frac{N_C}{N_A})^{3/5}\frac{2}{5}\frac{1-\frac{N_A}{N_C}}{1-(\frac{N_A}{N_C})^{2/5}} \tag{5-14}$$

For the diblock copolymer mixture described in this chapter, this ratio is about 1.87. This means that in the size distribution plots (figures 5-4 and 5-6), the population of mixed micelles overlaps with that of the 'pure' PS-PVP 75-18 micelles. The size of the mixed micelle is, naturally, in between of that for the 'pure' micelles, but closer to that of the small micelles. The ratio between the aggregation number of a mixed micelle and a 'pure' *A-B* micelle can be calculated by:

$$\frac{n_{mix}}{n_A} \sim \left(\frac{N_{eff}}{N_A}\right)^{4/5} \tag{5-15}$$

which is about 2.3 for the PS-PVP 75-18 / PS-PVP 75-102 mixture.

The fraction of long chains (*C-B*) in a mixed micelle is smaller than the fraction of short chains (*A-B*). For the case under consideration in this chapter, the fraction of long chains is given by $n_{CB}^{mix} / n_{mix} \approx 0.39$. When the difference in chain lengths increases, the fraction of long chains in mixed micelles decreases, tending to 0.22 for very long chains. This is shown in figure 5-7, where n_{CB}^{mix} / n_{mix} is plotted against N_C/N_A.

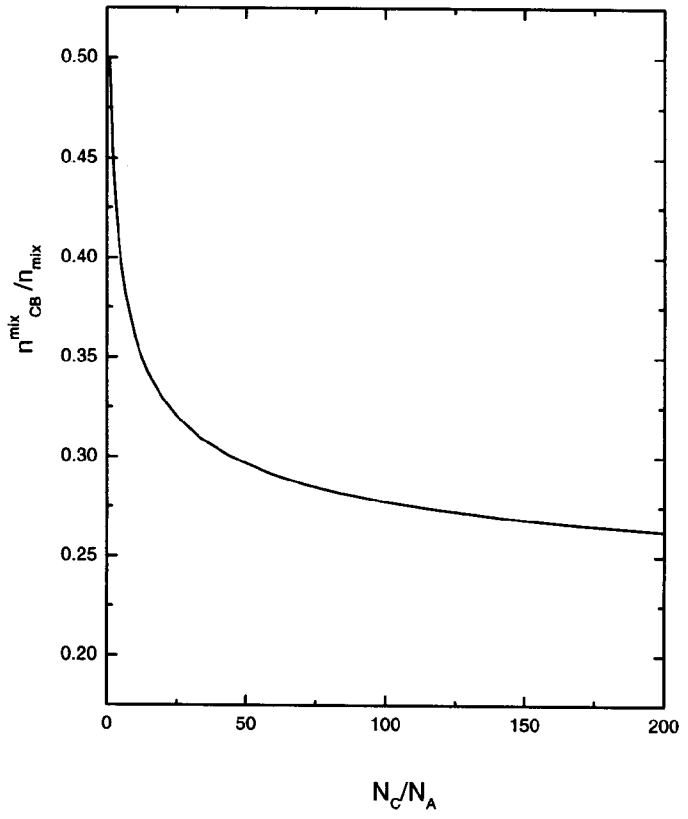

Figure 5-7. *Fraction of long chains in mixed micelles as a function of N_C/N_A.*

The incorporation of a long chain into a 'small' micelle leads to a decrease in extension of the blocks of the long chain in both core and corona regions, since the aggregation number of such a 'small' micelle is small. On the contrary, when a short chain enters a 'large' micelle, an additional extension of the blocks of the short chain occurs, since the radius and aggregation number of a 'large' micelle is large. This makes the formation of 'large' mixed micelles with participation of a few short chains unfavorable. Thus only 'small' mixed micelles consisting mainly of short chains with a small fraction of long chains will occur. Addition of long chains is possible until the increase in surface free energy reaches a certain limit.

The fraction of mixed micelles can also be estimated by minimization of the free energy (equation 5-1). The calculations lead to the following expression for the volume fraction of mixed micelles ϕ_{mix}:

$$\phi_{mix} \sim \phi_A^{(N_{eff}/N_A)^{4/5}} \exp\left[-\frac{3}{5}(N_{eff}\upsilon)^{6/5}\left(\frac{\gamma}{kT}\right)^{9/5}\left(1-\frac{5}{3}\left(\frac{N_A}{N_{eff}}\right)^{2/5}+\frac{2}{3}\left(\frac{N_A}{N_{eff}}\right)\right)\right] \tag{5-15}$$

where ϕ_A is the volume fraction of 'pure' *A-B* micelles.

As follows from equation 5-15, an increase of the fraction of long chains leads to an increase in the 'effective' chain length and as a result, the volume fraction of mixed micelles decreases. When the *C-B* chains are very long, the volume fraction of mixed micelles tends to zero and only 'pure' micelles are in solution. In such case the incorporation of a long chain into a small micelle results in a huge increase of micellar surface and mixed micelle formation becomes unfavorable. In the limit where $N_{eff} \rightarrow N_A$, the volume fraction of mixed micelles ϕ_{mix} tends to ϕ_A, i.e. the concentration of 'pure' A-B and mixed micelles becomes the same. In this limit, mixed and 'pure' micelles become identical.

For the mixture of PS-PVP 75-18 and PS-PVP 75-102 equation 5-15 becomes:

$$\phi_{mix} \sim \phi_A^{2.3} \exp\left[-0.172(N_{eff}\upsilon)^{6/5}\left(\frac{\gamma}{kT}\right)^{9/5}\right] \tag{5-16}$$

This means that the concentration of mixed micelles is much smaller than that of 'pure' PS-PVP 75-18 micelles.

Although the concentration of mixed micelles is presumably lower than that of 'pure' PS-PVP 75-18 micelles, the histograms in figures 5-4 and 5-6 reveal the formation of mixed micelles. From the peaks indicating the presence of 'small' micelles, whether they are 'pure' or mixed, an average value of about 21–22 nm for the diameter is found. This is clearly larger than the size of a pure PS-PVP 75-18 polymolecular micelle, which is determined to be about 15 nm. Using this value for calculating the size of a mixed micelle, an average size of about 28 nm is found. If it is assumed that 60% of the PS-PVP 75-18 chains are incorporated into 'pure' micelles and 40% into mixed micelles, the average size of the 'pure' and mixed micelles is about 22 nm. This is about the average size that can be obtained from figures 5-4 and 5-6. Even if the number of mixed micelles is three times smaller than that of 'pure' PS-PVP 75-18 micelles, an average size of about 19 nm is found for 'small' micelles, which is still in agreement with the experimentally found value.

This means that the experimental observed size distribution is not exactly bi-modal since besides the 'pure' micelles there are also mixed micelles. However, the mixed micelles and the 'pure' PS-PVP 75-18 micelles belong to the same peaks visible in the histograms shown in figures 5-4 and 5-6, resulting in an increase in average size for the 'small' micelles.

5.5 Conclusions

The behavior of a mixture of PS-PVP 75-18 and PS-PVP 75-102 diblock copolymers in toluene is investigated. At the first instance, mixed polymolecular micelles containing both diblock copolymer chains are formed and a broad distribution in micellar size is found. However, this broad variation in micellar size does not represent the equilibrium state. After aging for a couple of months, a quasi bi-modal distribution is detected. This is due to a re-distribution of the block copolymer chains over the polymolecular micelles. From theoretical predictions it is shown that for this system, mixed micelles can form in equilibrium having a size that is 1.87 times the size of a pure PS-PVP 75-18 polymolecular micelle. The fraction of PS-PVP 75-102 chains in mixed micelles is smaller than that of PS-PVP 75-18 chains and calculated to be 0.39. The experimentally found sizes are seen to correspond very well to the theoretical predictions. Furthermore, it has been predicted that the fraction of long chains in mixed micelles is decreasing when the ratio between the number of segments of the long and short chains in the block copolymer mixture is increasing.

5.6 References

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